

TITLE OF THE INVENTION

**STORAGE-STABLE FUEL CONCENTRATE**

INVENTORS

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## STORAGE-STABLE FUEL CONCENTRATE

### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

[0001] The present invention relates to a storage-stable concentrate for use with a fuel cell and a method of preventing or reducing the decomposition of a fuel for a liquid fuel cell during the storage thereof.

#### 2. Discussion of Background Information

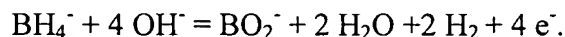
[0002] Fuel cells are electrochemical power sources wherein electrocatalytic oxidation of a fuel (e.g., molecular hydrogen or methanol) at an anode and electrocatalytic reduction of an oxidant (often molecular oxygen) at a cathode take place simultaneously. Conventional fuels such as hydrogen and methanol pose several storage and transportation problems, in particular, for portable fuel cells (e.g., for use with portable electric and electronic devices such as laptops, cell phones, and the like).

[0003] Borohydride- (and other hydride) based fuels are of particular interest for portable fuel cells, due to their very high specific energy capacity (see, e.g., J. of Electrochem. Soc., 150, (3), A398-402, 2003). This type of fuels may be used either directly as the fuel or indirectly as a generator of hydrogen (which is oxidized at the anode), e.g., as part of a portable proton exchange membrane (PEM) fuel cell (see, e.g., US 20010045364 A1, US 20030207160 A1, US 20030207157 A1, US 20030099876 A1, and U.S. Patent Nos. 6,554,877 B2 and 6,562,497 B2). The disclosures of all of the above documents are expressly incorporated herein by reference in their entireties.

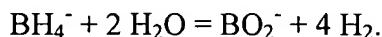
[0004] The main oxidation reaction of a borohydride compound at the anode of a fuel cell can be represented as follows:



[0005] However, there also is a side reaction which leads to hydrogen evolution during the electrocatalytic oxidation:



[0006] Moreover, during storage of a borohydride fuel, a spontaneous decomposition reaction usually takes place:



[0007] The above decomposition reaction results in not only an undesirable decrease of the specific energy capacity of the borohydride fuel, but also causes storage and transportation problems due to, in particular, the generation of (highly flammable) hydrogen gas, which may also lead to a dangerous increase of the pressure inside a fuel reservoir.

[0008] One of the factors which has a strong influence on the decomposition rate of a borohydride fuel and other metal hydride fuels is the temperature. With increasing temperature, the decomposition rate increases exponentially. Also, the presence of catalytic impurities (salts of Ni, Fe, Co, Mg, Ca, etc.) may significantly affect (increase) the fuel decomposition rate.

[0009] Increasing the alkalinity of a borohydride fuel and, in general, of hydride containing liquids for use with fuel cells is an inexpensive and effective way of increasing the stability thereof. However, increasing the alkalinity of the fuel to a level which affords a desirable fuel stability for storage and transportation purposes will usually entail an impractical increase in the fuel viscosity (i.e., such that pumping of the fuel becomes difficult or even impossible), a decrease in the solubility of reaction products in the fuel and/or a drop in the specific energy capacity of the fuel. In particular, for practical purposes the optimum hydroxide concentration in a fuel will usually be in the range of from about 3 to about 6 mole/liter. Compliance with storage and transportation regulations, on the other hand requires a fuel stability which will often be achievable only at hydroxide ion concentrations of about 8 mole/liter and higher.

#### SUMMARY OF THE INVENTION

[0010] The present invention provides a storage-stable liquid concentrate for use with a fuel cell. The concentrate comprises at least one metal hydride compound, a solvent which comprises one or more polar solvent components, and at least one hydroxide ion providing compound. After storage of the concentrate for 4 weeks at about 25 °C, not more than about 2 % of the at least one metal hydride compound will have decomposed.

[0011] In one aspect of the concentrate, the metal hydride compound may be capable of undergoing anodic oxidation in a liquid fuel cell and/or decomposition with generation of hydrogen gas under conditions which promote a hydrolysis thereof. Preferably, the at

least one metal hydride compound comprises a hydride, borohydride and/or aluminum hydride of an alkali metal and/or alkaline earth metal. By way of non-limiting example, the at least one metal hydride compound may comprise at least one of  $\text{NaBH}_4$ ,  $\text{KBH}_4$ ,  $\text{LiBH}_4$ ,  $\text{Be}(\text{BH}_4)_2$ ,  $\text{Ca}(\text{BH}_4)_2$ ,  $\text{Mg}(\text{BH}_4)_2$ ,  $(\text{CH}_3)_3\text{NHBH}_3$ ,  $\text{NaCNBH}_3$ ,  $\text{LiH}$ ,  $\text{NaH}$ ,  $\text{KH}$ ,  $\text{CaH}_2$ ,  $\text{BeH}_2$ ,  $\text{MgH}_2$ ,  $\text{NaAlH}_4$ ,  $\text{LiAlH}_4$ , and  $\text{KAlH}_4$ , preferably, at least one of  $\text{NaBH}_4$ ,  $\text{KBH}_4$ ,  $\text{LiBH}_4$ ,  $\text{LiH}$ ,  $\text{NaH}$ , and  $\text{KH}$ , e.g.,  $\text{NaBH}_4$  and/or  $\text{KBH}_4$ .

[0012] In another aspect, the concentrate may have a hydroxide ion concentration of at least about 7.5 moles per liter, e.g., at least about 8 moles per liter, and/or the concentrate may contain the at least one metal hydride compound in a concentration of at least about 3 moles per liter.

[0013] In yet another aspect, the at least one hydroxide ion providing compound may comprise at least one alkali or alkaline earth metal hydroxide and/or ammonium hydroxide. By way of non-limiting example, the at least one hydroxide ion providing compound may comprise at least one of  $\text{LiOH}$ ,  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{RbOH}$ ,  $\text{CsOH}$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{Mg}(\text{OH})_2$ ,  $\text{Ba}(\text{OH})_2$ , and  $\text{NH}_4\text{OH}$ , preferably,  $\text{NaOH}$  and/or  $\text{KOH}$ .

[0014] In a still further aspect, the solvent may comprise water, an aliphatic alcohol having up to about 6 carbon atoms and up to about 4 hydroxy groups, a  $\text{C}_{2-4}$  alkylene glycol, a di( $\text{C}_{2-4}$  alkylene) glycol, a mono- $\text{C}_{1-4}$ -alkyl ether of a  $\text{C}_{2-4}$  alkylene glycol or di( $\text{C}_{2-4}$  alkylene) glycol, a di- $\text{C}_{1-4}$ -alkyl ether of a  $\text{C}_{2-4}$  alkylene glycol or di( $\text{C}_{2-4}$  alkylene) glycol, an aliphatic ether having up to about 6 carbon atoms, an aliphatic ketone having up to about 6 carbon atoms, and/or a  $\text{C}_{1-3}$  alkyl ester of a  $\text{C}_{1-3}$  alkanolic acid. By way of non-limiting example, the solvent may comprise one or more of water, methanol, ethanol, ethylene glycol, diethylene glycol, glycerol, acetone, methyl ethyl ketone, diethyl ketone, methyl acetate, ethyl acetate, dioxan, tetrahydrofuran, diglyme and triglyme. The solvent may often comprise at least water.

[0015] In another aspect, the concentrate may comprise at least one of  $\text{NaBH}_4$  and  $\text{KBH}_4$  in a total concentration of at least about 4 moles per liter, water and  $\text{NaOH}$  and/or  $\text{KOH}$ .

[0016] In a still further aspect, the concentrate may essentially consist of  $\text{NaBH}_4$ ,  $\text{KBH}_4$ ,  $\text{LiBH}_4$ ,  $(\text{CH}_3)_3\text{NHBH}_3$ , and/or  $\text{NaCNBH}_3$ , a solvent which comprises water, and

NaOH and/or KOH, and may have a hydroxide ion concentration of at least about 8 moles per liter.

[0017] In yet another aspect, the concentrate, upon dilution thereof to a hydroxide ion concentration of not higher than about 6 moles per liter, may contain a sufficient amount of the metal hydride compound to be utilizable as a liquid fuel and/or a hydrogen generator for a fuel cell. By way of non-limiting example, when diluted to a hydroxide ion concentration of about 6 moles per liter, the concentrate may contain the metal hydride compound in a concentration of at least about 2 moles per liter, e.g., at least about 3 moles per liter.

[0018] In another aspect, the concentrate may be substantially free of any fuel additives which adversely affect the stability of the metal hydride compound. For example, it may be substantially free of plasticizers, detergents and antifreeze and/or it may be substantially free of stabilizers for the metal hydride compound.

[0019] In another aspect, not more than about 5 %, preferably not more than about 3 %, even more preferred, not more than about 2 % of the metal hydride compound will have decomposed after the concentrate has been kept for 1 year at about 25 °C.

[0020] The present invention also provides a process for preparing a metal hydride containing liquid for use in a fuel cell from a storage-stable concentrate. This process comprises combining a concentrate and a solvent in an amount of at least about 15 % by volume of the concentrate. The concentrate comprises at least one metal hydride compound and a polar solvent and has a hydroxide ion concentration of at least about 7 moles per liter. Also, not more than about 2 % of the metal hydride compound decomposes when the concentrate is kept for 4 weeks at about 25 °C.

[0021] In one aspect of the process, the combination of the concentrate and the solvent preferably affords a hydroxide ion concentration of the resultant mixture of not higher than about 6 moles per liter.

[0022] In another aspect of the process, preferably not more than about 0.5 % of the metal hydride compound decomposes when the concentrate is kept for 4 weeks at about 25 °C.

[0023] In another aspect, the hydroxide ion concentration in the concentrate may be at least about 7.5 moles per liter, e.g., at least about 8 moles per liter, and/or the

concentration of the at least one metal hydride compound is at least about 3 moles per liter.

[0024] In yet another aspect of the process, the metal hydride compound may comprise at least one of  $\text{NaBH}_4$ ,  $\text{KBH}_4$ ,  $\text{LiBH}_4$ ,  $\text{Be}(\text{BH}_4)_2$ ,  $\text{Ca}(\text{BH}_4)_2$ ,  $\text{Mg}(\text{BH}_4)_2$ ,  $(\text{CH}_3)_3\text{NHBH}_3$ ,  $\text{NaCNBH}_3$ ,  $\text{LiH}$ ,  $\text{NaH}$ ,  $\text{KH}$ ,  $\text{CaH}_2$ ,  $\text{BeH}_2$ ,  $\text{MgH}_2$ ,  $\text{NaAlH}_4$ ,  $\text{LiAlH}_4$ , and  $\text{KAlH}_4$ , preferably  $\text{NaBH}_4$  and/or  $\text{KBH}_4$ .

[0025] In a still further aspect, the concentrate may further comprise  $\text{LiOH}$ ,  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{RbOH}$ ,  $\text{CsOH}$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{Mg}(\text{OH})_2$ ,  $\text{Ba}(\text{OH})_2$ , and/or  $\text{NH}_4\text{OH}$ .

[0026] In yet another aspect of the process, the solvent may comprise at least one of water, methanol, ethanol, ethylene glycol, diethylene glycol, glycerol, acetone, methyl ethyl ketone, diethyl ketone, methyl acetate, ethyl acetate, dioxan, tetrahydrofuran, diglyme and triglyme.

[0027] In another aspect, the concentrate preferably comprises  $\text{NaBH}_4$  and/or  $\text{KBH}_4$ , water and  $\text{NaOH}$  and/or  $\text{KOH}$ .

[0028] In another aspect, a dilution of the concentrate to a hydroxide ion concentration of about 6 moles per liter will preferably result in a concentration of at least about 2 moles per liter of the at least one metal hydride compound.

[0029] The present invention also provides a process for providing a storage-stable packaged metal hydride containing liquid for use with a fuel cell. The liquid comprises at least one metal hydride compound and a polar solvent comprising a first portion and at least one second portion, and has a hydroxide ion concentration of not higher than about 7 moles per liter. The process comprises providing a container having a first compartment and at least one second compartment, partially or completely filling the first compartment with a concentrate which differs from the liquid (at least) in that it comprises only the first portion of the polar solvent and in that it has a hydroxide ion concentration of at least about 8 moles per liter, and partially or completely filling the at least one second compartment with the at least one second portion of the polar solvent.

[0030] In one aspect of the process, combining the contents of the first compartment with the contents of the at least one second compartment will preferably result in a hydroxide ion concentration of the combination of not higher than about 6 moles per liter.

[0031] In another aspect, preferably not more than about 1 % of the at least one metal hydride compound will decompose when the concentrate is kept for 4 weeks at about 25 °C.

[0032] In yet another aspect, the concentrate contains the at least one metal hydride compound in a concentration of at least about 3 moles per liter.

[0033] In a still further aspect of the process, the metal hydride compound may comprise at least one of  $\text{NaBH}_4$ ,  $\text{KBH}_4$ ,  $\text{LiBH}_4$ ,  $\text{Be}(\text{BH}_4)_2$ ,  $\text{Ca}(\text{BH}_4)_2$ ,  $\text{Mg}(\text{BH}_4)_2$ ,  $(\text{CH}_3)_3\text{NHBH}_3$ ,  $\text{NaCNBH}_3$ ,  $\text{LiH}$ ,  $\text{NaH}$ ,  $\text{KH}$ ,  $\text{CaH}_2$ ,  $\text{BeH}_2$ ,  $\text{MgH}_2$ ,  $\text{NaAlH}_4$ ,  $\text{LiAlH}_4$ , and  $\text{KAlH}_4$ .

[0034] In another aspect, the concentrate may further comprise at least one of  $\text{LiOH}$ ,  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{RbOH}$ ,  $\text{CsOH}$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{Mg}(\text{OH})_2$ ,  $\text{Ba}(\text{OH})_2$ , and  $\text{NH}_4\text{OH}$ .

[0035] In yet another aspect, the concentrate comprises  $\text{NaBH}_4$  and/or  $\text{KBH}_4$ , water, and  $\text{NaOH}$  and/or  $\text{KOH}$ .

[0036] In a still further aspect, the concentrate, when diluted to a hydroxide ion concentration of about 6 moles per liter, preferably contains at least about 2 moles per liter of the at least one metal hydride compound.

[0037] In another aspect, the container may be designed to allow a (i.e., at least some) mixing of the concentrate and the at least one second component of the polar solvent inside the container.

[0038] The present invention also provides a storage-stable packaged metal hydride containing liquid which is obtainable by the above process, including the various aspects thereof.

[0039] The present invention also provides a container that is filled with a metal hydride containing liquid. The container comprises a first compartment and at least one second compartment. The first compartment contains a concentrate which comprises at least one metal hydride compound and a polar solvent and has a hydroxide ion concentration of at least about 8 moles per liter. The at least one second compartment contains a solvent in an amount that is sufficient to result in a hydroxide ion concentration of not higher than about 7 moles per liter for the mixture of the solvent in the at least one second compartment and the concentrate in the first compartment.

**[0040]** In one aspect, the container may be sealed and allow a mixing of the concentrate and the at least one second component of the polar solvent before discharging same from the container. The container may even be associated with instructions to allow the concentrate and the at least one second component of the polar solvent to mix before discharging same from the container.

**[0041]** In another aspect, the container may comprise an internal partition which defines the first compartment and the at least one second compartment. By way of non-limiting example, the first compartment may be surrounded, at least partially, by the at least one second compartment, or the at least one second compartment may be at least partially surrounded by the first compartment.

**[0042]** In yet another aspect of the container, the amount of the solvent in the at least one second compartment may be sufficient to result in a hydroxide ion concentration of not higher than about 6 moles per liter for the mixture of the solvent in the at least one second compartment and the concentrate in the first compartment.

**[0043]** In a still further aspect, the concentrate may contain the at least one metal hydride compound in a concentration of at least about 3 moles per liter.

**[0044]** In yet another aspect, the metal hydride compound may comprise at least one of  $\text{NaBH}_4$ ,  $\text{KBH}_4$ ,  $\text{LiBH}_4$ ,  $\text{Be}(\text{BH}_4)_2$ ,  $\text{Ca}(\text{BH}_4)_2$ ,  $\text{Mg}(\text{BH}_4)_2$ ,  $(\text{CH}_3)_3\text{NHBH}_3$ ,  $\text{NaCNBH}_3$ ,  $\text{LiH}$ ,  $\text{NaH}$ ,  $\text{KH}$ ,  $\text{CaH}_2$ ,  $\text{BeH}_2$ ,  $\text{MgH}_2$ ,  $\text{NaAlH}_4$ ,  $\text{LiAlH}_4$ , and  $\text{KAlH}_4$ , and/or the concentrate may further comprises at least one of  $\text{LiOH}$ ,  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{RbOH}$ ,  $\text{CsOH}$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{Mg}(\text{OH})_2$ ,  $\text{Ba}(\text{OH})_2$ , and  $\text{NH}_4\text{OH}$ . By way of non-limiting example, the concentrate may comprise  $\text{NaBH}_4$  and/or  $\text{KBH}_4$ , water, and  $\text{NaOH}$  and/or  $\text{KOH}$ .

**[0045]** In another aspect of the container of the present invention, the concentrate, when diluted to afford a hydroxide ion concentration of about 6 moles per liter, may contain the metal hydride compound in a concentration of at least about 2 moles per liter, e.g., at least about 3 moles per liter.

**[0046]** The present invention also provides a refilling device for a liquid fuel cell. This device comprises the container of the present invention, including the various aspects thereof.

**[0047]** In one aspect, the device may be designed to be capable of accommodating a spent liquid from a liquid fuel cell.



[0048] The present invention also provides a packaged combination for providing a metal hydride containing liquid for use with a fuel cell. The combination comprises a first container and at least one second container. The first container contains a concentrate which comprises at least one metal hydride compound, a polar solvent, and at least one hydroxide ion providing compound, and has a hydroxide ion concentration of at least about 8 moles per liter. The at least one second container contains a solvent in an amount sufficient to result in a hydroxide ion concentration of not higher than about 7 moles per liter for a mixture of the solvent in the at least one second container and the concentrate in the first container.

[0049] In one aspect, the combination may be associated with instructions to combine the concentrate in the first container with at least a part of the solvent from the second container. In another aspect of the combination, the concentrate may comprise  $\text{NaBH}_4$  and/or  $\text{KBH}_4$ , water, and  $\text{NaOH}$  and/or  $\text{KOH}$ .

[0050] In a still further aspect of the combination, the solvent in the at least one second container may contain an additive for the fuel which is preferably selected from plasticizers, detergents, stabilizers for the at least one metal hydride compound (e.g., an aliphatic or aromatic amine) and/or antifreeze.

[0051] The present invention also provides a method of reducing the decomposition of a fuel for a liquid fuel cell during storage of the fuel. This method comprises keeping the fuel in the form of the above-discussed concentrate, including the various aspects thereof, and diluting the concentrate to prepare the fuel only shortly before the use of the fuel in a fuel cell.

[0052] The storage-stable liquid concentrate of the present invention comprises several components. In this regard, it is noted that the recitation of these components herein and in the appended claims must not be construed to mean that these components are necessarily present as such in the concentrate. Rather, those of skill in the art will understand that these components may have been starting materials in the preparation of the concentrate and may have reacted to form new species by reaction and/or interaction with other starting materials and/or components of the concentrate.

[0053] The metal hydride compound for use in the concentrate of the present invention preferably is a compound which can be oxidized as such at the anode of a fuel cell to

provide electrons and/or can (at least) be used as a generator of molecular hydrogen which in turn is usable as a fuel in a fuel cell, e.g., by hydrolysis of the metal hydride compound. It is to be understood that the term "metal hydride compound" as used in the present specification and the appended claims is used in a broad sense and encompasses, in particular, compounds which are "simple" hydrides, such as, e.g., NaH, KH, etc. as well as compounds which comprise a hydride complex ion such as, e.g., borohydride, aluminum hydride and the like. Non-limiting examples of metal hydride compounds for use in the present invention include hydrides, borohydrides, including cyanoborohydrides, and aluminum hydrides of alkali metals such as, e.g., Li, Na, K, Rb and Cs, and alkaline earth metals such as, e.g., Be, Mg, Ca, Sr and Ba, but also of organic cations such as, e.g., mono-, di-, tri- and tetraalkylammonium ions. Corresponding specific compounds include, but are not limited to,  $\text{LiBH}_4$ ,  $\text{NaBH}_4$ ,  $\text{KBH}_4$ ,  $\text{Be}(\text{BH}_4)_2$ ,  $\text{Ca}(\text{BH}_4)_2$ ,  $\text{Mg}(\text{BH}_4)_2$ ,  $(\text{CH}_3)_3\text{NHBH}_3$ ,  $\text{NaCNBH}_3$ ,  $\text{LiH}$ ,  $\text{NaH}$ ,  $\text{KH}$ ,  $\text{CaH}_2$ ,  $\text{BeH}_2$ ,  $\text{MgH}_2$ ,  $\text{NaAlH}_4$ ,  $\text{LiAlH}_4$ , and  $\text{KAlH}_4$ . Borohydrides and, in particular,  $\text{NaBH}_4$  and  $\text{KBH}_4$  are preferred for the purposes of the present invention.

[0054] The solvent which constitutes another component of the concentrate of the present invention comprises one or more polar (protic and/or aprotic) solvent components. If the solvent is a pure solvent, i.e., there is only one solvent component, it must be polar. If the solvent is a solvent mixture, i.e., comprises one or more (e.g., two, three, four, or even more) individual solvents, at least one of the components of the mixture must be polar. Preferably, all or at least substantially all of the solvent components are polar. Solvents and solvent mixtures for use in the present invention preferably are liquid at room temperature and are preferably present in an amount which is sufficient to dissolve at least a part (and preferably, all) of the metal hydride compound(s) and the hydroxide ion providing compound(s). Non-limiting examples of suitable solvents include water, mono- and polyhydric alcohols (e.g., methanol, ethanol, propanol, isopropanol, butanol, and glycerol) and mono- and polyalkylene glycols (such as, e.g., ethylene glycol, diethylene glycol, propylene glycol, and dipropylene glycol), aliphatic esters of mono- and polycarboxylic acids (e.g., ethyl acetate, methyl acetate, ethyl formate, and diethyloxalate), aliphatic ketones (such as, e.g., acetone, methyl ethyl ketone, and diethylketone) and (cyclo)aliphatic ethers (such as tetrahydrofuran, dioxane

and partial or complete alkyl esters of mono- and polyhydric alcohols and mono- and polyalkylene glycols). A preferred solvent component is water, at least as long as the metal hydride compound does not react to any substantial extent with protic solvents. Other preferred solvent components include monohydric and polyhydric aliphatic and cycloaliphatic alcohols such as methanol and ethanol.

[0055] The hydroxide ion providing compound for use in the concentrate of the present invention may be any compound which is capable of providing hydroxide ions in the concentrate, e.g., by dissociation, decomposition, or by (*in situ*) reaction or interaction with any other compound that may be present in the concentrate. It will be understood that these compounds must not interfere to any significant extent with the operation of the fuel cell and, in particular, the electrochemical reactions that take place therein. Usually, the hydroxide ion providing compound will include at least one alkali or alkaline earth metal hydroxide and/or ammonium hydroxide. Non-limiting specific examples of suitable compounds are LiOH, NaOH, KOH, RbOH, CsOH, Ca(OH)<sub>2</sub>, Mg(OH)<sub>2</sub>, Ba(OH)<sub>2</sub>, and NH<sub>4</sub>OH. The corresponding oxides, carbonates and bicarbonates are non-limiting examples of further compounds which may serve as hydroxide ion providing compounds. Often, NaOH and/or KOH will be employed. The amount of the hydroxide ion providing compound(s) is apparently dependent on the desired hydroxide ion concentration in the concentrate.

[0056] The concentrate of the present invention is storage-stable, i.e., after storing the concentrate for 4 weeks at about 25 °C, not more than about 2 mole-%, preferably not more than about 1 %, e.g., not more than about 0.5 %, not more than about 0.25 %, or not more than about 0.1 % of the metal hydride compound will have decomposed. Moreover, after storing the concentrate for 1 year at about 25 °C, preferably not more than about 5 %, e.g., not more than about 3 %, e.g., not more than about 2 %, not more than about 1 %, or even not more than about 0.5 % of the metal hydride compound(s) will have decomposed (calculated on a molar basis).

[0057] The hydroxide ion concentration in the concentrate that will provide the desired stability depends, *inter alia*, on the specific metal hydride compound(s), the solvent(s) and the amounts thereof, and the presence or absence of fuel additives and the like that may have an adverse effect on the stability of the metal hydride compound(s). Generally

speaking, the hydroxide ion concentration in the concentrate will usually be higher than about 6 moles per liter, but will usually not be higher than about 14 moles per liter, preferably, not higher than about 12 moles per liter. Usually, the hydroxide ion concentration in the concentrate will be at least about 7 moles per liter, preferably at least about 7.5 moles per liter, even more preferred at least about 8 moles per liter, e.g., at least about 8.5 moles per liter, at least about 9 moles per liter, or even at least about 10 moles per liter.

[0058] The desirable concentration of the metal hydride compound(s) in the concentrate of the present invention is somewhat related to the hydroxide ion concentration in the concentrate. In particular, because the concentrate is intended to be used, in diluted form, as fuel/hydrogen generator for a fuel cell, the higher the hydroxide ion concentration in the concentrate and the lower the desired hydroxide ion concentration in the diluted concentrate (i.e., the fuel/hydrogen generator), the higher is the preferred concentration of the metal hydride compound(s) in the concentrate. In other words, after dilution of the concentrate to a desired hydroxide ion concentration, the resulting liquid should still contain a sufficient concentration of metal hydride compound(s) to be useful as fuel/hydrogen generator for a fuel cell. While the useful concentration of metal hydride compound(s) will depend, *inter alia*, on the fuel cell and the capacity thereof, as well as on many other factors, the concentrate of the present invention will usually contain the metal hydride compound(s) in a concentration which after dilution of the concentrate to a hydroxide ion concentration of about 6 mole/liter, affords a concentration of the metal hydride compound(s) of at least about 0.5 mole/liter, preferably at least about 1 mole/liter, or at least about 2 mole/liter, e.g., at least about 3 mole/liter, at least about 4 mole/liter, or even at least about 5 mole/liter. In general, the (total) concentration of the metal hydride compound(s) in the concentrate will often be in the range of from about 4 mole/liter to about 12 mole/liter.

[0059] In order to further increase the stability of the concentrate of the present invention, it is preferred for the concentrate to be substantially free of any substances which adversely affect the stability of the metal hydride compound(s) contained therein. For example, it may be desirable to have additives present in the fuel/hydrogen generator for the fuel cell, such as, e.g., one or more plasticizers, detergents and antifreeze. The

concentrate of the present invention is preferably free of such additives or contains only minor quantities thereof (e.g., a total of less than about 0.1 % by weight, even more preferred, less than about 0.01 % by weight). It is also preferred for the concentrate to not contain any substances other than the metal hydride compound(s), the solvent or solvent components, respectively, and the hydroxide ion providing compound(s). If other substances are present, their total concentration preferably does not exceed about 5 % by weight, and preferably does not exceed 1 % by weight. Unless otherwise indicated, the weight percentages given herein are based on the total weight of the concentrate. Should it be desired for the final fuel/hydrogen generator to contain any substances which preferably are not present in the concentrate (or at least not in the desired concentrations), they may be added to the concentrate shortly before or during the dilution thereof. For example, all or a part of these desired substances may be added to the liquid (solvent) that is used for the dilution of the concentrate (i.e., the diluent). It may, in particular, be advantageous to add one or more stabilizers for the metal hydride compound(s) to the diluent, because the diluted concentrate may no longer have a sufficiently high hydroxide ion concentration to satisfactorily stabilize the metal hydride compound over extended periods of time. Non-limiting examples of suitable stabilizers include aromatic and aliphatic amines. Non-limiting examples of other additives such as, e.g., plasticizers, detergents and antifreeze include polyhydric alcohols such as, e.g., glycerol and ethylene glycol (antifreeze). Of course, in many cases the latter compounds may as well be present as the diluent (polar solvent) or a component thereof.

**[0060]** The diluent for use with the concentrate of the present invention will usually comprise one or more of the solvent components that are present in the concentrate, in the same or a different ratio (preferably, in the same ratio) as in the concentrate. The diluent may also contain at least one different solvent component, or may be composed entirely of one or more solvents which are not present in the concentrate. Of course, in the latter case particular care must be taken that the one or more solvents of the diluent are compatible with the one or more solvent components, the hydroxide ion providing compound(s) and, in particular, the metal hydride compound(s) of the concentrate. In particular, the diluent should preferably not cause any substantial precipitation when the diluent is combined with the concentrate. The diluent will usually not contain any metal

hydride compound(s). Also, it will usually contain no hydroxide ion providing compound(s) or, if it does, in a concentration which is significantly lower than the hydroxide ion concentration in the concentrate. However, as already set forth above, the diluent may contain additives and other materials whose presence in the fuel is desirable but which may affect the (long-term) stability of the metal hydride compound in the concentrate. A suitable amount of diluent for its combination with the concentrate is dependent on various factors, *inter alia*, the hydroxide ion concentration in the concentrate and the desired hydroxide ion concentration of the diluted concentrate (i.e., the fuel/hydrogen generator). Usually, the amount of diluent will be at least about 15 % by volume of the concentrate, often at least about 20 % by volume, e.g., at least about 30 % by volume, at least about 40 % by volume, or at least about 50 % by volume.

[0061] There are various possible ways of providing a combination of the concentrate and the diluent therefor for commercial purposes. For example, the combination may be provided in a single container, or in at least two separate containers, one containing the concentrate and the other one containing at least (and, preferably, exactly) the amount of diluent needed for bringing the concentrate to the desired final concentration. In the latter case, the contents of the at least two containers may be combined outside and/or inside the fuel cell, optionally by means of a mixing device.

[0062] If the concentrate and the diluent are provided in a single container, the container may have various designs. The container should be capable of substantially preventing direct liquid-liquid contact between the concentrate and the diluent. By way of non-limiting example, the container may comprise two chambers or compartments which share a partition, or the chambers or compartments may be completely separated from each other (i.e., no shared structural element). The outlets of these compartments may be connected inside the container and/or merge into a common outlet opening of the container. Alternatively, the container may be designed to allow a substantially complete mixing of the contents of the compartments while the concentrate and the diluent are still inside the container. For example, the partition between the compartment that contains the concentrate and the compartment that contains the diluent may be movable and/or removable (preferably, while the container is still closed). Furthermore, a valve may be provided between these compartments. Alternatively, the partition (e.g., a membrane)

may be ripped open (e.g., by bending or squeezing the container) or otherwise rendered unsuitable for preventing a direct contact between the concentrate and the diluent (e.g., by piercing, use of a slide fastener, e.g., a ridge-and-channel "zipper" of the Ziploc® variety, etc.) inside the container. Of course, once the concentrate has been diluted (i.e., combined with the diluent) it should preferably be discharged from the container without undue delay, because the stability of the diluted concentrate, in particular, the metal hydride compound(s) contained therein may no longer be suitable for long-term or intermediate-term storage.

[0063] Particularly preferred containers (e.g., refill cartridges for a fuel cell) for use with the concentrate of the present invention (and a diluent therefor) are described in a copending application having the title Refilling System for a Fuel Cell and Method of Refilling a Fuel Cell (inventors: Gennadi Finkelshtain, Mark Estrin, Moti Meron, Rami Hashimshoni and Erik Torgeman; Attorney Docket No.: P24757), filed concurrently herewith. The disclosure of this application is expressly incorporated by reference herein in its entirety.

#### DETAILED DESCRIPTION OF THE PRESENT INVENTION

[0064] The particulars shown herein are by way of example and for purposes of illustrative discussion of the embodiments of the present invention only and are presented in the cause of providing what is believed to be the most useful and readily understood description of the principles and conceptual aspects of the present invention. In this regard, no attempt is made to show structural details of the present invention in more detail than is necessary for the fundamental understanding of the present invention, the description making apparent to those skilled in the art how the several forms of the present invention may be embodied in practice.

##### **Example 1**

[0065] 22.4 g of KOH (Frutarom Ltd.) is dissolved in 80 ml of deionized water and cooled to room temperature. 15.12 g of  $\text{NaBH}_4$  is dissolved in the resultant solution with stirring for 30 min. Then water is added to a final volume of 100 ml. This solution contains 4 M KOH and 4 M  $\text{NaBH}_4$ . The solution (100 ml) is placed in a flask and

equilibrated at 70 °C for 10 minutes to obtain thermostatic conditions. Thereafter, the evolution of hydrogen is measured by determining the amount of displaced water. The hydrogen evolution rate is determined to be 1.42 ml/min.

### **Example 2**

[0066] Example 1 is repeated with the exception that 44.8 g of KOH and 30.24 g of NaBH<sub>4</sub> are used, resulting in a solution containing 8 M KOH and 8 M NaBH<sub>4</sub>. The hydrogen evolution rate is determined to be 0.053 ml/min.

[0067] In parallel, 50 ml of a solution of 8 M KOH and 8 M NaBH<sub>4</sub> is mixed with 50 ml of deionized water. The hydrogen evolution rate is determined to be the same as that in Example 1. Thus, a twofold increase in the concentration of KOH results in an about 25-fold increase in the stability of the NaBH<sub>4</sub>.

### **Example 3**

[0068] 18 g of KOH (Frutarom Ltd.) is dissolved in 65 ml of deionized water and cooled to room temperature. 19.5 g of KBH<sub>4</sub> is dissolved in the resultant solution with stirring for 30 min. Then water is added to a final volume of 100 ml. This solution contains 3.2 M KOH and 3.6 M KBH<sub>4</sub>. The solution (100 ml) is placed in a flask and equilibrated at 70 °C for 10 minutes to obtain thermostatic conditions. Thereafter, the evolution of hydrogen is measured by determining the amount of displaced water. The hydrogen evolution rate is determined to be 0.23 ml/min.

### **Example 4**

[0069] 36 g of KOH (Frutarom Ltd.) is dissolved in 30 ml of deionized water and cooled to room temperature. 39 g of KBH<sub>4</sub> is dissolved in the resultant solution with stirring for 30 min. Then water is added to a final volume of 100 ml. This solution contains 6.4 M KOH and 7.2 M KBH<sub>4</sub>. The solution (100 ml) is placed in a flask and equilibrated at 70 °C for 10 minutes to obtain thermostatic conditions. Thereafter, the evolution of hydrogen is measured by determining the amount of displaced water. The hydrogen evolution rate is determined to be 0.01 ml/min.



[0070] In parallel, 50 ml of a solution of 6.4 M KOH and 7.2 M  $\text{KBH}_4$  is mixed with 50 ml of deionized water. The hydrogen evolution rate is determined to be the same as that in Example 3. Thus, a twofold increase in the concentration of KOH results in an about 23-fold increase in the stability of the  $\text{KBH}_4$ .

#### Example 5

[0071] 14.11 g of KOH and 6.72 g of NaOH (Frutarom Ltd.) are dissolved in 60 ml of deionized water and cooled to room temperature. 12.7 g of  $\text{NaBH}_4$  is dissolved in the resultant solution with stirring for 30 min. Then water is added to a final volume of 100 ml. This solution contains 2.5 M KOH, 1.7 M NaOH and 3.4 M  $\text{NaBH}_4$ . The solution (100 ml) is placed in a flask and equilibrated at 70 °C for 10 minutes to obtain thermostatic conditions. Thereafter, the evolution of hydrogen is measured by determining the amount of displaced water. The hydrogen evolution rate is determined to be 0.45 ml/min.

#### Example 6

[0072] 28.22 g of KOH and 13.44 g NaOH (Frutarom Ltd.) are dissolved in 30 ml of deionized water and cooled to room temperature. 25.4 g of  $\text{NaBH}_4$  is dissolved in the resultant solution with stirring for 30 min. Then water is added to a final volume of 100 ml. This solution contains 5 M KOH, 3.4 M NaOH and 6.8 M  $\text{NaBH}_4$ . The solution (100 ml) is placed in a flask and equilibrated at 70 °C for 10 minutes to obtain thermostatic conditions. Thereafter, the evolution of hydrogen is measured by determining the amount of displaced water. The hydrogen evolution rate is determined to be 0.024 ml/min.

[0073] In parallel, 50 ml of a solution of 5 M KOH, 3.4 M NaOH and 6.8 M  $\text{NaBH}_4$  is mixed with 50 ml of deionized water. The hydrogen evolution rate is determined to be the same as that in Example 5. Thus, a twofold increase in the concentration of KOH and NaOH results in an about 19-fold increase in the stability of the  $\text{NaBH}_4$ .

#### Example 7

[0074] 18.5 g of KOH (Frutarom Ltd.) is dissolved in 60 ml of deionized water and cooled to room temperature. 15 g of  $\text{NaBH}_4$  is dissolved in the resultant solution with

stirring for 30 min. Then water is added to a final volume of 100 ml. This solution contains 3.3 M KOH and 4 M NaBH<sub>4</sub>. The solution (100 ml) is placed in a flask and equilibrated at 70 °C for 10 minutes to obtain thermostatic conditions. Thereafter, the evolution of hydrogen is measured by determining the amount of displaced water. The hydrogen evolution rate is determined to be 1.07 ml/min.

#### **Example 8**

[0075] 18.5 g of KOH (Frutarom Ltd.) is dissolved in 60 ml of deionized water and cooled to room temperature. 15 g of NaBH<sub>4</sub> is dissolved in the resultant solution with stirring for 30 min. Then 10 ml of glycerol and water are added to a final volume of 100 ml. This solution contains 3.3 M KOH and 4 M NaBH<sub>4</sub>. The solution (100 ml) is placed in a flask and equilibrated at 70 °C for 10 minutes to obtain thermostatic conditions. Thereafter, the evolution of hydrogen is measured by determining the amount of displaced water. The hydrogen evolution rate is determined to be 3.2 ml/min.

[0076] Thus, the addition of glycerol results in a decrease in the thermal stability of the NaBH<sub>4</sub> by a factor of about 3. However, glycerol decreases the freezing point of the mixture, wherefore it may be desirable to use it as fuel additive and incorporate it in a diluent.

[0077] It is noted that the foregoing examples have been provided merely for the purpose of explanation and are in no way to be construed as limiting of the present invention. While the present invention has been described with reference to exemplary embodiments, it is understood that the words which have been used herein are words of description and illustration, rather than words of limitation. Changes may be made, within the purview of the appended claims, as presently stated and as amended, without departing from the scope and spirit of the present invention in its aspects. Although the present invention has been described herein with reference to particular means, materials and embodiments, the present invention is not intended to be limited to the particulars disclosed herein; rather, the present invention extends to all functionally equivalent structures, methods and uses, such as are within the scope of the appended claims.